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A cleaner production of synthesis gas from glycerol using thermal water steam plasma

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ABSTRACT

Glycerol, which is a by-product of biodiesel production, is considered to be a potential feedstock for synthesis gas generation. Therefore, the objective of this study was to investigate the use of thermal water steam plasma as one of the potential thermochemical technologies for cleaner production, to reform glycerol into the synthesis gas. A direct current plasma torch stabilized by a mixture of argon-steam vortex and operating at atmospheric pressure was used to produce active radicals. The reforming of glycerol was carried out at various flow rates of steam, glycerol, and plasma torch power. The modeling of chemical processes was also proposed. The reaction products were mostly gases with the concentrations as follows: hydrogen 47%, carbon monoxide 25.2%, carbon dioxide 12%, methane 5.4%, and acetylene 1.7%. The reforming system was quantified in terms of carbon conversion, hydrogen and carbon monoxide yield, and hydrogen/carbon monoxide ratio as well as energy efficiency and specific energy requirement. This study indicates that synthesis gas with a high content of hydrogen and carbon monoxide could be effectively produced from glycerol through the thermal water steam plasma reforming.

1. Introduction

Due to limited fossil fuel reserves, crude-oil price variations and international regulations on emissions, the use of new, renewable and cleaner energy sources has received a significant attention. In the recent years, renewable and carbon dioxide neutral biomass derived fuels have been recognized as a potential alternative source of fuels. In particular, the global production of biofuels (biodiesel) from biomass is growing continually (The Renewable Fuels Agency (RFA), 2010). The production of biodiesel is expected to increase in the European Union, as well as in the Member State Lithuania, in order to meet the goal of replacing 20% and 30% of petroleum-based fuels with biofuels by 2020 and 2030, respectively (Diyauddeen et al., 2012; EU Directive 2009/28/EC, 2009). This would lead to an increase in glycerol yield and induce a higher supply than demand in the different industrial areas such as chemical, food, cosmetic, and pharmaceutical. Therefore, it is expected that a great amount of excess glycerol will be available on the market. The biodiesel production in Lithuania in 2014 increased by ~25% compared to 2013 (from 118 thousand tons to 147 thousand tons), whereas the total EU27 biodiesel production in 2014 increased sharply by 123% compared to 2013 and was over 23 mln. tons (European Biodiesel Board (EBB), 2015). Hence, the amount of crude glycerol, which is theoretically expected to be 10 wt% (practically even up to 30%) as a by-product after the production of one ton of biodiesel, has increased significantly. The excess crude glycerol will become an issue from both economic and environmental perspectives. For this reason, a new application of crude glycerol should be proposed.

Glycerol, which is a by-product of biodiesel production, is considered a potential feedstock for renewable and cleaner energy production. Albarelli et al. (2011) states that energy production from glycerol is a very promising field due to its non-toxicity, low vapor pressure, low flammability and high energy density characteristics. The utilization possibilities of crude glycerol for synthesis gas and/or hydrogen production through various techniques have been reported in a number of investigations: Valliyappan et al.

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(2008) pyrolyzed glycerol at 650–800 °C with a carrier nitrogen gas for the production of clean fuels such as H_2 and syngas; Fernandez et al. (2009) carried out the pyrolysis of glycerol over a selected activated carbon, which resulted in an elevated gas fraction with a higher $H_2 + CO$ composition; Huang et al. (2014) used metal oxides-modified Ni-based catalysts for glycerol steam reforming to syngas. The catalyst helped to improve glycerol conversion to syngas and inhibited water–gas shift reaction and methanation, but was rapidly deactivated due to carbon deposition; Pompeo et al. (2010) applied platinum catalysts on different supports for steam reforming of glycerol at temperatures lower than 450 °C. A strong support effect on the behavior of catalysts was determined; Rennard et al. (2009) explored the catalytic partial oxidation (CPOx) of glycerol to syngas using noble-metal catalysts such as rhodium and platinum. They found that rhodium catalysts produce equilibrium selectivity to syngas, while platinum catalysts produce mainly autothermal non-equilibrium products; Davda et al. (2005) used aqueous-phase reforming (APR) process to produce hydrogen or alkanes in high yields over different metals; Kunkes et al. (2009) used an integrated carbon-supported Pt-based bimetallic catalyst for the production of hydrogen by glycerol reforming coupled with water–gas-shift reaction. They reported that this integrated catalytic system may serve as an energy-efficient approach to produce hydrogen from biomass-derived feedstocks; Chen and Lin (2013) produced hydrogen and synthesis gas from activated carbon and steam via reusing carbon dioxide; Ortiz et al. (2012) proposed a conceptual design for reforming glycerol using supercritical water to produce maximum electrical power in an energy self-sufficient system; Lin (2013) summarized the methods (pyrolysis, steam reforming, partial oxidation, autothermal reforming, and aqueous-phase reforming) of glycerol valorization to hydrogen or syngas, indicating that heterogeneous catalysis plays a critical role in converting glycerol into valuable chemicals such as hydrogen and syngas. However, the methods mentioned above have some drawbacks, including catalyst sensitivity to contaminants and its deactivation, expensive materials such as Pt used for catalysts preparation, high investment and exploitation costs, requirement of external high-temperature heat sources, inducing thermal absorption reaction, requirement of high pressures, pretreatment of crude glycerol, etc.

As an alternative, plasma-based technologies have drawn attention as a new cleaner method to overcome such limitations. According to Huang and Tang (2007), two main groups of plasmas can be distinguished: the high temperature, or fusion, plasmas and the low temperature plasmas. The low temperature plasmas may further be divided into thermal plasmas in which a quasi-equilibrium state between electrons and ions is fulfilled, and cold plasmas characterized by a non-equilibrium state. Mostly thermal plasmas are usually applied for toxic waste treatment, metallurgical processes, materials synthesis, etc., while non-thermal plasmas are used for surface treatment (cleaning, sterilization, deodorization, etching), gas treatment (ozonation, VOC's removal, etc.) (Tendero et al., 2006).

Recently, the thermal plasma technology has been started to be applied for organic waste treatment, especially for waste-to-energy and/or waste-to-product. Bosmans et al. (2013) reviewed the existing waste-to-energy treatment technologies, indicating that the plasma gasification/vitrification is an advanced and a viable candidate for combined energy and material valorization. Furthermore, a few attempts to convert glycerol to valuable secondary products by plasma technology were investigated by (Yoon et al., 2013; Zhu et al., 2009). Thermal plasma differs from incineration in the sense that it may be used for recovering not only the energy but also the chemical value of the waste. The conversion of waste into secondary energy carriers allows for a cleaner production. The thermal plasma enables generating radicals and reactive species which can considerably accelerate chemical reactions (Sekiguchi and Mori, 2003). Therefore, plasma itself could be considered as a catalyst with the properties such as the high density of energy, high chemical reactivity, and very high temperatures (10^3–10^4 K). However, the method has some drawbacks. In case of arc torches used, periodic replacement of the plasma torch electrodes is required, or, in case of radio frequency (RF) and microwave (MW) induced plasma, expensive power supply sources are needed. Furthermore, the latter efficiency is lower as compared to arc plasma torches (Bonizzoni and Vassallo, 2002). Tang et al. (2013) compared different type of plasma generators and stated that an RF plasma has some drawbacks such as a difficult ignition and an easy extinction under some operating conditions. While easy ignition and running more stably are the prominent advantage of a DC plasma. Besides, the commercial viability of plasma technologies (DC, RF, MW, DC–RF) for waste treatment has not yet been proven. On the other hand, the life cycle assessment of conventional and advanced energy-from-waste technologies, such as a two-stage gasification–plasma process for waste treatment, shows better environmental performances over conventional waste treatment technologies (Evangelisti et al., 2015).

In this study, the use of thermal arc discharge plasma to reform glycerol to synthesis gas was investigated. Steam was used as the plasma-forming gas, which makes the process even cleaner, because the formation of NO_x is avoided as in the case of air used as the plasma-forming gas. For the convenient interpretation of the reforming characteristics and the known chemical composition, pure glycerol was used instead of crude glycerol. The effects of different reforming parameters such as the steam flow rate, glycerol flow rate, and plasma torch power were studied. The modeling of chemical processes, based on a classical thermodynamic equilibrium reactor (TER), was also proposed. The TER model showed quite a good agreement between calculated and experimental data for the case of H_2, giving a relative deviation of 6%, whereas the difference for the case of CO was 17%. Furthermore, a quantification of the reforming system in terms of energy efficiency and specific energy requirement was performed. It was found that synthesis gas with a high content of H_2 and CO could be effectively produced from glycerol through the thermal water steam plasma reforming. The glycerol reforming to synthesis gas strongly depended on the steam/glycerol ratio as well as the plasma torch power. As the steam/glycerol ratio increased at the plasma torch power of 56 kW, the best reaction performance was obtained.

2. Experimental SETUP and methods

2.1. Design of the glycerol reforming system

In this study, steam reforming of glycerol was carried out using a plasma-chemical reactor. The experimental system designed for the glycerol reforming is shown in Fig. 1. It consists of an atmospheric pressure DC arc plasma torch, a power supply system, a steam generator, a superheater, a gas supply system, a chemical reactor, a glycerol supply system, a condenser, and a gas chromatograph. The plasma-chemical reactor used in this study was 1 m long with the 0.4 m inner diameter. The plasma torch is mounted on top of the reactor, and the nozzles for the glycerol supply are installed perpendicularly to the downstream plasma flow. At the bottom of the reactor, there is a section for the removal of char and condensed water, and in the middle an outlet chamber for the produced gaseous products is installed. Pure glycerol (99.5%) was used as a substitute for crude glycerol. The glycerol was supplied to the plasma-chemical reactor from the cylinder at constant rates of 2 g s^{-1} and 4 g s^{-1}, respectively, through special